**Experiment 4 (**Future - Lab needs an unknown)

## USING A pH TITRATION TO DETERMINE THE ACID CONTENT OF SOFT DRINKS

2 lab periods

*Reading: Chapter 9, 185-197; Chapter 10, pg 212-218; Chapter 14 pg 317-323, Quantitative Chemical Analysis, 8th Edition, Daniel C. Harris (7th Edition: Chapter 10, 181-191; Chapter 11, pg 206-218; Chapter 15 pg 306-311).*

### Objective

This lab will introduce you to the concept of pH titrations. You will use the pH electrode to find the end points for the titrations of two polyprotic acids, citric acid and phosphoric acid, with a strong base. You will use this information to determine the phosphoric acid and citric acid concentrations in two different types of soft drinks.

### Suggested Schedule

Work in groups of two for this experiment. One student will complete the titration of a cola drink, and the other student will complete the titration of the uncola drink.

Lab 1 Prepare and standardize your 0.1 M NaOH solution, if required. Familiarize yourself with the care and use of the pH electrode and meter. Begin titration of soda samples.
Lab 2 Finish titration of soda samples.

Phosphoric acid ($H_3PO_4$), a triprotic acid, is a common ingredient in cola drinks. It provides a taste that is both sweet and sour, but does not compete with other flavors. The concentration of phosphoric acid in cola drinks is dependent on pH:

$$H_3PO_4 + OH^- = H_2PO_4^- + H_2O$$
$$H_2PO_4^- + OH^- = HPO_4^{2-} + H_2O$$
$$HPO_4^{2-} + OH^- = PO_4^{3-} + H_2O$$

In this experiment, we will determine the $H_3PO_4$ and $H_2PO_4^-$ concentrations in a sample of a cola drink using a potentiometric titration. We choose a potentiometric detection method over an acid-base indicator for two reasons: (1) the color of the cola obscures indicator changes, and (2) the use of a pH meter permits a more accurate location of the end points in a titration than does an indicator.

We will also determine the citric acid concentration in a non-cola soft drink. Citric acid, which is also tribasic, is another common ingredient in many soft drinks. The acid dissociation constants for phosphoric and citric acids are as follows:

| | **Phosphoric acid** | **Citric acid** |
|---|---|---|
| $\mathbf{K_{a1}}$ | $7.11 \times 10^{-3}$ | $7.44 \times 10^{-4}$ |
| $\mathbf{K_{a2}}$ | $6.32 \times 10^{-8}$ | $1.73 \times 10^{-5}$ |
| $\mathbf{K_{a3}}$ | $7.10 \times 10^{-13}$ | $4.02 \times 10^{-7}$ |

From these data, it is clear that the acid dissociation constants for phosphoric acid are more than a factor of 1,000 apart. Thus, three distinct endpoints can be observed in the titration of phosphoric acid. In contrast, the acid dissociation constants for citric acid are closer together, and the individual endpoints are very difficult to observe. Since some of the citric and phosphoric acid endpoints are close to each other, it will be *very* difficult to observe distinct titration endpoints if a soft drink containing *both* citric acid and phosphoric acid (Pepsi is one example) is used for this experiment. If you would like to bring in your own soft drinks, choose ones that have *either* phosphoric acid *or* citric acid, and not both in their ingredient list. The drinks also should not contain lactic acid or aspartame (Nutrasweet) so do not choose diet drinks! Lactic acid and aspartame both have carboxylic acid groups and may interfere with the endpoint determination.

The glass electrode you will use in this experiment responds selectively to $H^+$. If you turn the pH electrode upside down, you will see a thin glass membrane in the shape of a bulb surrounded by a plastic "shield wall". The membrane is the pH sensitive part of the electrode. The difference in $[H^+]$ inside the electrode and outside in the solution produces a voltage difference across the glass membrane. This potential difference, $E_{glass}$ is related to the pH of the solution through the following equation:

$$E_{glass}\ (\text{mV}) = -59.16\ \beta\ pH + k$$

where $k$ and $\beta$ are constants. Note the similarity of the relationship between $E_{glass}$ and pH to that beween y and x in the equation for a straight line, y = mx + b. As you can see, there is a simple linear relationship between the measured electrode potential and the pH of the solution. When the electrode is calibrated with two (or sometimes three) buffers, $E_{glass}$ can be directly related to pH.

You will calibrate the pH electrode with pH 4, 7, and 10 buffers. When you calibrate an electrode with standard buffers, you measure a potential (E) with the electrode in each buffer. For two buffers, B1 and B2, having pH values of $pH_1$, and $pH_2$, the pH meter calculates a linear calibration line between two points. The slope of the line is given by:

$$slope = \frac{E_{B2} - E_{B1}}{pH_2 - pH_1}$$

To determine the pH of an unknown solution, the potential ($E_{unk}$) of that solution is measured with a calibrated electrode. Then, the pH is determined by substitution:

$$\frac{E_{unk} - E_{B1}}{pH_{unk} - pH_1} = \frac{E_{B2} - E_{B1}}{pH_2 - pH_1}$$

The pH meter software is typically programmed to do the calculations required for calibration. The pH meter software also determines the pH of the unknown solution for you. In this experiment you will use the Vernier LabQuest as a pH meter. Once the calibration procedure is complete, you can simply read the pH from the meter.

The Vernier LabQuest is only capable of doing a *two-point* calibration, or a calibration with two buffers at a time. Thus, you must first calibrate the electrode between pH 4 and 7, and then

calibrate it between 7 and 10 once you reach the appropriate point in your titration. It is important to do a separate calibration for each region of the titration, because different sets of standards will give calibration lines having different slopes. For example, a calibration using pH 7 and pH 10 buffers will give a calibration line with a slope that is different from that of a calibration line acquired using pH 4 and pH 7 buffers. Ideally, the pH of your unknown solution is bracketed by the two buffer pH values. This is not possible for us below pH 4, however. Once the electrode is calibrated, the pH of the $H_3PO_4$ or citric acid solution is easily followed as a function of added NaOH.

At pH 10.5 – 11, the glass electrode begins to respond to other ions (mainly $Na^+$ in this case), since so few $H^+$ ions remain. This effect, which makes it appear that the pH is lower than it really is, is called the *alkaline error*. The alkaline error makes it advisable not to carry the titration beyond pH 10.5, meaning that you will not observe the third equivalence point of phosphoric acid.

***Prelaboratory Assignment***

The phosphoric acid in a 125.00-mL sample of cola drink was titrated with 0.1323 M NaOH. If the first end point occurred after 13.55 mL of base was added, and the second end point occurred after 29.78 mL of base, calculate the concentrations of $H_3PO_4$ and $H_2PO_4^-$ in the cola sample. (Hint: where would the second equivalence point have occurred if only $H_3PO_4$ were present?)

## Apparatus

- Stir plate and stir bar
- Vernier LabQuest and pH electrode
- 100-ml, 250-mL, 400-mL beakers
- 50-mL buret
- 25-mL volumetric pipet
- 1000-mL bottle
- 25-mL graduated cylinder
- 1000-mL flask for boiling water
- Stirring rod
- Watch glass

## Chemicals

- Sodium hydroxide. A 50% wt/wt solution of NaOH will be provided by Lab Services.
- KHP primary standard. This will be provided by Lab Services.
- Cola unknown (*e.g.*, Coca Cola). You may bring your own sodas, if you desire.
- Uncola unknown (*e.g.* Squirt)
- pH 4, 7 and 10 buffers—provided.
- Phenolphthalein indicator—provided.
- Containers for ice baths—provided.

## Procedure

*The combination pH electrodes you will use in this experiment are very expensive. Please handle them with care! The pH sensitive part of the electrode is the thin glass membrane in the shape of a bulb at the bottom end of the electrode. This glass membrane is very fragile, and one must be careful not to damage it. If you use a stir bar in your solution during your titration, be sure the electrode is in a location to one side of the beaker where it cannot be damaged by the stir bar. It is best if the electrode is somewhat high in the beaker, but still below the level of the solution. Never touch the membrane, and never apply pressure to it. To dry the bulb, carefully wick the excess liquid away using a Kim Wipe. The TA's will demonstrate this technique.*

*The pH electrode has most likely been soaking in a solution prepared by lab services. Remove it from this solution, rinse and dry carefully, then allow it to soak in pH 7 buffer solution while you are preparing your 0.1 M NaOH solution and your samples.*

### I Calibration Procedure

*In order for the pH electrode to give accurate measurements, it must be calibrated with buffer solutions having known pH values. The buffers you are given are traceable to standards developed at, and disseminated by, the National Institute of Standards and Technology (NIST). Use the following steps to calibrate the pH electrode.*

1. Plug the cable of the pH electrode into the Vernier LabQuest.
2. Wash the electrode carefully with DI water by directing a stream of water from a squirt bottle at the bulb. Wick away excess liquid using the procedure demonstrated by the TA.
3. Place the electrode in enough pH 7 buffer solution to completely cover the glass bulb. On the screen of the Lab Quest, press "sensors"→ "calibrate" → "pH" → "calibrate now". Swirl or stir the solution while taking the reading. When the voltage reading on the top right of the screen stabilizes, enter 7.00 under reading 1. Press "keep".

   *Note: You must always start a pH calibration procedure with the pH 7 buffer solution.*

4. Remove the electrode from the pH 7 buffer solution, rinse it, wick away excess liquid, and place it in the pH 4 buffer solution. Again, swirl or stir the solution while taking the reading. When the voltage reading stabilizes, enter 4.00 under reading 2. Press keep. Press ok. Check to make sure the pH reading of the pH 4 buffer is really 4.00 and the pH reading of the pH 7 buffer is really 7.00. pH readings may vary by ±0.03 or so pH units.

   *You have now completed a "two point calibration", which means your pH readings are fairly accurate as long as the pH is between ~4 and 7.*

   *If your pH readings are very different from what they should be, recalibrate the electrode. If that does not work, ask Lab Services for another electrode.*

   *Once the pH of the solution you are titrating reaches 7 you will need to recalibrate using buffer solutions of 7 and 10, respectively.*

5. Rinse the probe again with DI water, wick away excess liquid, and begin your experiment.

## II Preparation and standardization of a 0.1 M NaOH solution.

1. Prepare and standardize a 0.1 M NaOH solution, as you did in Experiment 1. For *one* of the *three* standardization titrations, use your pH electrode in conjunction with the phenolphthalein indicator and compare the electrode response to the indicator color change. Do this even if you have already standardize the NaOH solution.

   *You may wish to set up the apparatus with a buret stand. One buret clamp can hold your buret and another clamp can hold the electrode. The beaker will sit on a stir plate. Make sure your electrode is submersed in solution, but it needs to be in a position where it cannot be damaged by the stir bar. Turn up the stir speed slowly and carefully to start the stir bar in motion.*

   Add small increments of titrant, noting both the pH value and the total volume of NaOH after each addition. Initially, the additions should be large enough to cause pH changes of about 0.2 units. When the pH starts to change rapidly, reduce the size of the NaOH aliquots. *Do not forget to recalibrate your pH electrode once you have reached a pH of ~7.* As you near the end point, the pH will change considerably with even the slightest addition of base. To develop the entire titration curve (pH vs. volume of titrant), you will need to proceed somewhat beyond the end point. The electrode response is going to be the principal indicator of the endpoint in this experiment, but you should observe that the indicator changes color at the point where the greatest pH change occurs (note this volume). Any difference between where the indicator changes color and the true equivalence point is called the indicator error, which should be small. Stop the titration at pH 10.5.

*Note:* *The pH readings may take a little time to stabilize after each addition of base. A stable reading is one which does not change or only fluctutates by ± 0.1 pH unit. Wait for readings to stabilize before noting the pH.*

## III Titration of Phosphoric Acid and Citric Acid in Soft Drinks

1. Add ~400 mL of soda to a 600-mL beaker. Cover the beaker with a clean watch glass.
2. Bring your sample solution just to boiling and keep it that way for ~5-10 minutes. This expels the $CO_2$, which otherwise would interfere with the titration. Cool the solution by placing cold water (you may want to use an ice bath) in an appropriate container and carefully resting the beaker with the soda in the cold water.
3. Pipet 100.00 mL of your cooled soda solution into a 250-mL beaker.
4. Calibrate your pH electrode using pH 7 and 4 buffer solutions, if you have not already done so. Rinse the electrode with DI water, wick dry, and place it in the beaker containing the soda sample, making sure the electrode is submersed in the soda. Add the stir bar and *slowly* turn up the speed on the stir plate. Measure the pH of your solution.
5. Refill your buret with the 0.1 M NaOH solution. Proceed with the titration of the soda solution as you did for the NaOH standardization (except that there is no indicator here). Once the pH of the solution you are titrating reaches 7, you will need to recalibrate using buffer solutions of 7 and 10 respectively. Continue to pH 10.5.

6. Repeat steps 3–5 twice more. Make sure to provide your partner with a copy of your data.

   *Recall that you should expect two equivalence points for the cola titration, one near pH 4 and the other near pH 8. For the "uncola" only one equivalence point, near pH 6, should be found.*

**IV. Titration of Performance Standard**

1. Day Three of this Lab.
2. Obtain an unknown phosphoric acid sample from lab services.
3. Determine its concentration.

**Calculations/Questions**

1. Calculate the concentration of the NaOH titrant from your KHP titrations.
2. Using Excel, or a similar plotting program, create separate titration curves for the titration of KHP and each of the two soda samples. This is accomplished by plotting pH (ordinate, *i.e*, y-axis) vs. volume of NaOH (abscissa, *i.e.*, x-axis) for each set of data. Indicate on the plots a) the buffer region(s), b) the region(s) where pH = pKa, c) the end point(s), d) the region where $OH^-$ is in excess, and e) the major species present in solution in each region.
3. Again using Excel, or a similar plotting program, construct first-derivative plots for these titrations. Follow the procedure described on pages 208-211 of your text. A first-derivative plot is constructed by plotting $(pH_2 - pH_1)/(V_2 - V_1)$ vs. $(V_1 + V_2)/2$, where $V_1$ and $V_2$ are two successive titration volumes (totals) and $pH_1$ and $pH_2$ are the two corresponding pH values. Create a table as shown in the report template, Part B. The first derivative plots will have peaks where the original graphs have inflection points (i.e. the end points of the titrations). See Figure 10-5 on page 215 of your text for an example. Determine the end points for each titration from these plots. Compare the results you obtained from the first derivative plot for the KHP titration with the results you obtained using the phenolphthalein indicator. What is your indicator error? Is it significant? Which technique seems to be the most accurate in terms of standardizing your NaOH solution? What are the benefits/drawbacks of each technique? Determine the average end point and associated uncertainty for the cola and for the uncola solutions.
4. Use the end point volumes obtained for the cola titration, along with the NaOH concentration, to calculate moles of $H_3PO_4$ present. Remember that at the first equivalence point one proton has been titrated, while at the second equivalence point, two protons have reacted. If your results show that $V_{eq2} > 2\ V_{eq1}$, then not only $H_3PO_4$ but also $H_2PO_4^-$ was in present in the drink (see Prelab Assignment). Calculate the concentrations of both. Could $V_{eq2} < 2V_{eq1}$ ? Explain. Assuming you could titrate to the third equivalence point, what would the relationship be between $V_{eq1}$, $V_{eq2}$, and $V_{eq3}$?
5. Calculate the concentration of citric acid in the uncola.
6. In this experiment you both used an indicator and a graphical method (the derivative plot) to determine the end point of a titration. Describe some strengths and weaknesses of these methods. Describe a second graphical method that can be used to determine the end point of a titration. What is the benefit of using this method?

**Experiment 4** Name _____

***Potentiometric Analysis of Acid in Soft Drinks: Cola vs. Uncola***

*Purpose*

*Calculations*

**A. Standardization of NaOH**

Mean conc. NaOH solution: _____*M*

Standard deviation: _____ *M*

Relative standard deviation (%RSD): _____%

**B. Data for titration of cola and uncola with NaOH**

Using Excel or a similar program, make a table with the following columns:

| Vol. NaOH Added | pH | $V_2 - V_1$ | $pH_2 - pH_1$ | $(V_1 + V_2)/2$ | $\frac{pH_2 - pH_1}{V_2 - V_1}$ |
|---|---|---|---|---|---|
| | | | | | |

**C. Results**

**Cola:** pH of soda after boiling:_____

Volume NaOH required to reach first end point: _____±_____ml; pH: _____

Volume NaOH required to reach second end point: _____±_____ml; pH: _____

$H_3PO_4$ concentration: _____±_____*M* %RSD:_____

$H_2PO_4^-$ concentration:_____ ±_____*M* %RSD:_____

**Uncola:** pH of soda after boiling:_____

Volume NaOH required to reach the end point: _____±_____ml; pH: _____

Citric acid concentration: _____±_____*M* %RSD:_____

***Include all information from the Calculations/Questions section as well as sample calculations; answer all questions. Check your calculations carefully! Don't forget to include copies of your lab notebook pages for this experiment.***